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(54) Bleaching composition for machine dishwashing

(57) A bleaching composition adapted for use in machine dishwashing having reduced silver-tarnishing and enhanced glassware pattern protection properties, as well as good cleaning performance contains a silicate-based alkalinity system containing a minor proportion of sodium metasilicate and has a pH measured as a 1% solution of said composition at 20°C of from 9.0 to 11.5.

GB 2 295 625 A

BLEACHING COMPOSITIONS

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Technical Field

The present invention relates to bleaching compositions, adapted for use in machine dishwashing, exhibiting good bleachable stain removal, reduced silver-tarnishing and enhanced glassware pattern protection properties.

Background to the Invention

Compositions designed for use in automatic dishwasher machines are well known, and a consistent effort has been made by detergent manufacturers to improve the cleaning and/or rinsing efficiency of said compositions on chinaware, glassware and silverware, as reflected by numerous patent publications.

The present invention is, in one aspect, concerned with the silver-tarnishing problem encountered when compositions which contain oxygen-bleaching species are employed in machine dishwashing methods.

The satisfactory removal of bleachable soils such as tea, fruit juice and coloured vegetable soils, such as carotenoid soils is a particular challenge to the formulator of a machine dishwashing composition. Traditionally,

the removal of such soils has been enabled by the use of bleach components such as oxygen and chlorine bleaches.

A problem encountered with the use of such bleaches is the tarnishing of any silverware components of the washload. Oxygen bleaches tend to give rise to the problem of tarnishing more than chlorine bleaches. The level of tarnishing observed can range from slight discolouration of the silverware to the formation of a dense black coating on the surface of the silverware.

The formulator thus faces the dual challenge of formulating a product which maximises bleachable soil cleaning but minimises the occurrence of tarnishing of silverware components of the washload.

It has been found that reduced silver tarnishing as well as good cleaning performance can be achieved through the use in an oxygen bleach containing formulation of a silicate-based alkalinity system containing both sodium silicate having an $SiO_2 : Na_2O$ ratio of from 1.8 to 3.0 and a minor proportion of sodium metasilicate. The formulation should have a pH of from 9.0 to 11.5.

To further reduce the occurence of silver tarnishing, the rate of release of the oxygen bleach is preferably also controlled. The rate of release of oxygen bleach is preferably rapid enough to provide satisfactory cleaning, but not so rapid that tarnishing is enabled.

The use of such a silicate-based alkalinity system has also been found to reduce the level of any corrosion of any glass patterning on the glassware in the wash. Such glass patterning typically comprises coloured glass having a high lead oxide (PbO) content, of typically 50%, a silicate content of about 30% and often additionally other metal ions such as cadmium and barium. Glass patterning corrosion has been found to be a particular problem for patterned glassware washed in phosphate builder containing machine dishwashing formulations.

It has further been found that the total level of SiO_2 should be carefully adjusted. In particular, the use of too high levels of SiO_2 in a formulation can lead to problems associated with permanent clouding and iridescence

on the surface of any glassware, including coloured and opaque glassware, in the wash.

It has also been found that where the composition contains a silicate-based alkalinity system containing both sodium silicate having an SiO_2 : Na_2O ratio of from 1.8 to 3.0 and a minor proportion of sodium metasilicate an unexpected reduction in the formation of calcium carbonate films on the articles in the wash may be observed in both and hard and soft water conditions versus a similar silicate-based alkalinity system containing no metasilicate.

Phosphate-built machine dishwashing compositions having a high pH, of generally greater than 12, which contain high levels of metasilicate are known in the art, and for example are disclosed in US-A-3,708,427, US-A-4,528,039, US-A-4,457,322, and DE-A-4128672. The compositions of the invention by contrast have a pH of from 9.0 to 11.5 and much lower levels of metasilicate, in combination with a silicate having an SiO_2 : Na_2O ratio of from 1.8 to 3.0, and also a lower total SiO_2 level.

Machine dishwashing compositions of lower pH, containing silicates are also known. For example, GB-B-2,206,601 discloses machine dishwashing compositions generally having a pH of from 9.5 to 11.5. At page 10, it is stated that mixtures of silicates and metasilicates can be used. An Example is given of a phosphate-built composition having a metasilicate content of greater than12%. Also, European Patent Applications EP-A-516,554 and EP-A-516,555 disclose phosphate-built machine dishwashing compositions having a pH <11.0, which contain from 3 to 30% silicate. Both sodium disilicate and sodium metasilicate are stated to be preferred. None of these references however, recognize the utility of the specific silicate-based alkalinity system of the invention, which has, as an essential aspect, only a minor proportion of sodium metasilicate.

PCT Patent Application No. WO92/13061 discloses a process for producing a solid cast silicate-based cleansing composition. Examples are provided therein, at page 24, Table 1, of trial compositions containing both a sodium silicate having an SiO_2:Na_2O ratio of 2.4 and a minor proportion of sodium metasilicate. The total level of SiO_2 present in these

compositions is however significantly higher than that envisaged by the present invention, which recognizes that high SiO_2 levels can give rise to clouding and iridescence problems. No pH is stated for the trial compositions, but given the presence, at relatively high levels, of sodium hydroxide, it would be expected to be substantially more alkaline than the compositions of the present invention. No disclosure in this reference relates to silver tarnishing or glass pattern protection. The problem addressed is, by contrast, related to the derivation of effective processing routes for silicate-based tablet detergent products.

It is an object of the present invention to provide compositions, suitable for use in machine dishwashing methods, having reduced silver-tarnishing and enhanced glassware pattern protection properties, as well as good cleaning performance, particularly bleachable soil removal performance.

Summary of the Invention

There is provided a bleaching composition, adapted for use in a machine dishwashing method, containing

(a) an oxygen-releasing bleaching system;

(b) sodium silicate having an $SiO_2 : Na_2O$ ratio of from 1.8 to 3.0, present at a level of from 0.5% to 20% SiO_2 by weight ; and

(c) sodium metasilicate, present at a level of at least 0.4% SiO_2 by weight

wherein the weight ratio of said sodium silicate to said sodium metasilicate, measured as SiO_2, is from 50:1 to 3:2 and wherein the pH of a 1% solution of said composition measured at 20°C is from 9.0 to 11.5.

Detailed Description of the Invention

The present compositions contain as essential components an oxygen-releasing bleach and a silicate-based alkalinity system containing sodium

silicate having an SiO_2 : Na_2O ratio of from 1.8 to 3.0 and a minor proportion of sodium metasilicate.

Machine dishwashing compositions

The bleaching compositions herein are adapted for use in a machine dishwashing method. Such compositions are formulated to enable the removal of, typically food based, soils and stains from soiled tableware under the conditions present in a machine dishwasher. Typically the compositions are low foaming, preferably containing only low levels of low-foaming surfactants.

Oxygen-releasing bleaching system

The first essential feature of the invention is an oxygen-releasing bleaching system. In a preferred aspect the bleaching system comprises a hydrogen peroxide source and a peroxyacid bleach precursor compound. The production of the peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Suitable sources of hydrogen peroxide include inorganic perhydrate bleaches.

Inorganic perhydrate bleaches

The compositions in accord with the invention preferably include a hydrogen peroxide source, as an oxygen-releasing bleach. Suitable hydrogen peroxide sources include the inorganic perhydrate salts.

The inorganic perhydrate salts are normally incorporated in the form of the sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular

compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Sodium percarbonate, which is a preferred perhydrate for inclusion in compositions in accordance with the invention, is an addition compound having a formula typically corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in product stability.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4.n.Na_2CO_3$ wherein n is form 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Another suitable, and preferred, coating material contains sodium silicate having an SiO_2:Na_2O of from 1.8 to 3.0 and/or sodium metasilicate. Where present as a coating material, such sodium silicate and/or sodium metasilicate can perform three functions, namely: enhancing storage stability of the perhydrate salt, delaying dissolution of the perhydrate salt and hence release of hydrogen peroxide to the wash solution, and providing SiO_2 to the wash solution as part of the alkalinity system in accord with the invention.

Other coatings which contain silicate (alone or with borate salts or boric acids or other inorganics), waxes, oils, fatty soaps can also be used advantageously within the present invention.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Peroxyacid bleach precursor

Peroxyacid bleach precursors are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the compositions.

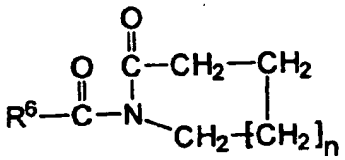
Suitable peroxyacid bleach precursors typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Suitable peroxyacid bleach precursor compounds include the N-acylated lactams, perbenzoic acid and perbenzoic acid derivative precurosrs, peroxyacid precursors and alkyl fatty acid precursor compounds described in more detail hereinafter.

N-acylated lactam precursor compound

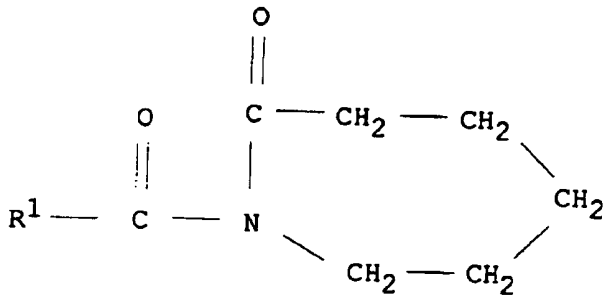
N-acylated precursor compounds of the lactam class are disclosed generally in GB-A-855735. Whilst the broadest aspect of the invention contemplates the use of any lactam useful as a peroxyacid precursor, preferred materials comprise the caprolactams and valerolactams.

Suitable N-acylated lactam precursors have the formula:



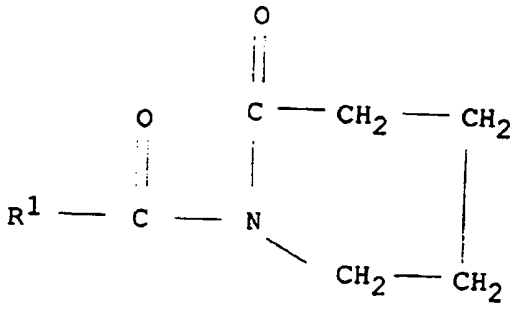
wherein n is from 0 to about 8, preferably from 0 to 2, and R^6 is H, an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons, or a substituted phenyl group containing from 6 to 18 carbon atoms

Suitable caprolactam bleach precursors are of the formula:



wherein R^1 is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms, most preferably R^1 is phenyl.

Suitable valero lactams have the formula:



wherein R^1 is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R^1 is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

The most preferred materials are those which are normally solid at <30°C, particularly the phenyl derivatives, ie. benzoyl valerolactam, benzoyl

caprolactam and their substituted benzoyl analogues such as chloro, amino alkyl, alkyl, aryl and alkoxy derivatives.

Caprolactam and valerolactam precursor materials wherein the R^1 moiety contains at least 6, preferably from 6 to 12, carbon atoms provide peroxyacids on perhydrolysis of a hydrophobic character which afford nucleophilic and body soil clean-up. Precursor compounds wherein R^1 comprises from 1 to 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of 'hydrophobic' and 'hydrophilic' caprolactams and valero lactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

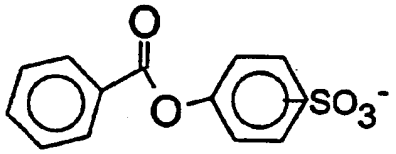
Highly preferred caprolactam and valerolactam precursors include benzoyl caprolactam, nonanoyl capro-lactam, benzoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl caprolactam, 3,5,5-trimethylhexanoyl valerolactam, octanoyl caprolactam, octanoyl valerolactam, decanoyl caprolactam, decanoyl valerolactam, undecenoyl caprolactam, undecenoyl valerolactam, (6-octanamidocaproyl)oxybenzene-sulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)-oxybenzenesulfonate, and mixtures thereof. Examples of highly preferred substituted benzoyl lactams include methylbenzoyl caprolactam, methylbenzoyl valerolactam, ethylbenzoyl caprolactam, ethylbenzoyl valerolactam, propylbenzoyl caprolactam, propylbenzoyl valerolactam, isopropylbenzoyl caprolactam, isopropylbenzoyl valerolactam, butylbenzoyl caprolactam, butylbenzoyl valerolactam, tert-butylbenzoyl caprolactam, tert-butylbenzoyl valerolactam, pentylbenzoyl caprolactam, pentylbenzoyl valerolactam, hexylbenzoyl caprolactam, hexylbenzoyl valerolactam, ethoxybenzoyl caprolactam, ethoxybenzoyl valerolactam, propoxybenzoyl caprolactam, propoxybenzoyl valerolactam, isopropoxybenzoyl caprolactam, isopropoxybenzoyl valerolactam, butoxybenzoyl caprolactam, butoxybenzoyl valerolactam, tert-butoxybenzoyl caprolactam, tert-butoxybenzoyl valerolactam, pentoxybenzoyl caprolactam, pentoxybenzoyl valerolactam, hexoxybenzoyl caprolactam, hexoxybenzoyl valerolactam, 2,4,6-trichlorobenzoyl caprolactam, 2,4,6-trichlorobenzoyl valerolactam,

pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl caprolactam, dimethoxybenzoyl caprolactam, 4-chlorobenzoyl caprolactam, 2,4-dichlororbenzoyl caprolactam, terephthaloyl dicaprolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl valerolactam, dimethoxybenzoyl valerolactam, 4-chlorobenzoyl valerolactam, 2,4-dichlororbenzoyl valerolactam, terephthaloyl divalerolactam, 4-nitrobenzoyl caprolactam, 4-nitrobenzoyl valerolactam, and mixtures thereof.

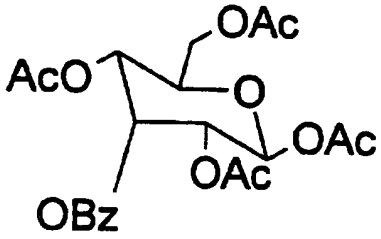
Perbenzoic acid precursor

Essentially any perbenzoic acid precursors are suitable herein, including those of the N-acylated lactam class, which are preferred.

Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, including for example benzoyl oxybenzene sulfonate:



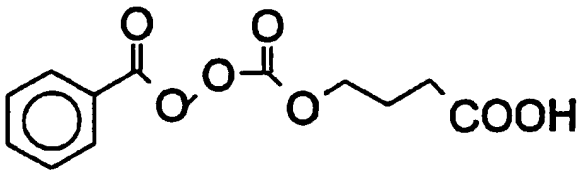
Also suitable are the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, including for example:



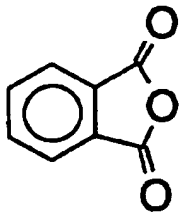
Ac = COCH3; Bz = Benzoyl

Preferred perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Preferred perbenzoic acid precursors include the benzoyl diacyl peroxides, the benzoyl tetraacyl peroxides, and the compound having the formula:



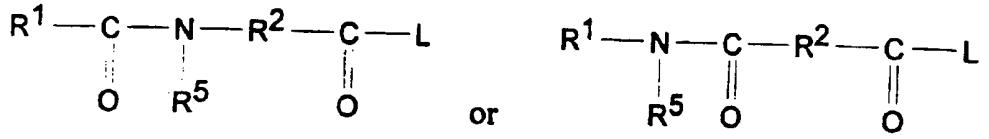
Phthalic anhydride is another suitable perbenzoic acid precursor compound herein:



Perbenzoic acid derivative precursors

Suitable perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the perbenzoic group is substituted by essentially any functional group including alkyl groups.

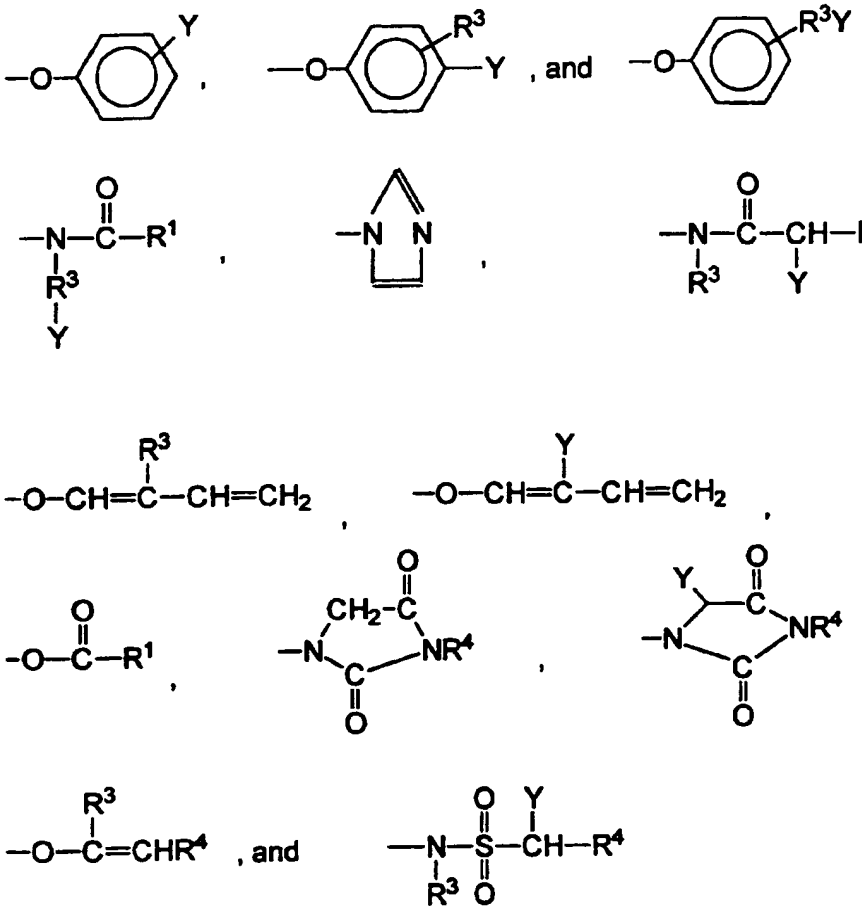
Another preferred class of substituted perbenzoic acid precursor compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an aryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be aryl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

The L group must be sufficiently reactive for the reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. These characteristics are generally paralleled by the pKa of the conjugate acid of the leaving group, although exceptions to this convention are known. Ordinarily, leaving groups that exhibit such behaviour are those in which their conjugate acid has a pKa in the range of from 4 to 13, preferably from 6 to 11 and most preferably from 8 to 11.

Preferred bleach precursors are those wherein R^1, R^2 and R^5 are as defined for the amide substituted compounds and L is selected from the group consisting of:



and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group.

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<-N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing groups should be

well dispersed in the bleaching solution in order to assist in their dissolution.

Cationic peroxyacid precursors

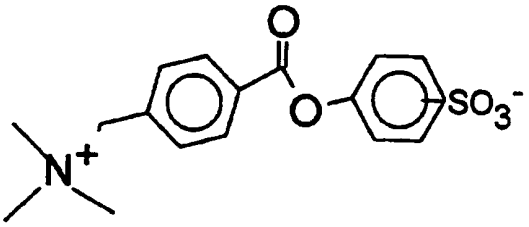
Cationic peroxyacid precursor compounds are also suitable herein. Typically such cationic peroxyacid precursors are formed by substituting the peroxyacid part with an ammonium or alkyl ammmonium group, preferably an ethyl or methyl ammonium group.

Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

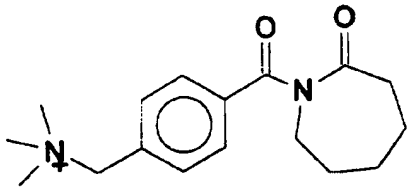
Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:



A preferred cationically substituted alkyl oxybenzene sulfonate is the methyl ammonium derivative of 2,3,3-tri-methyl hexanoyloxybenzene sulfonate.

Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:



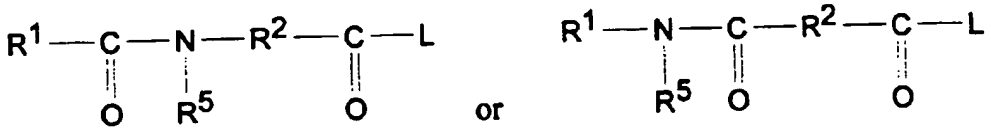
Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

Alkyl fatty peroxyacid bleach precursors

Alkyl fatty peroxyacid bleach precursors form alkyl fatty peroxyacids on perhydrolysis. Preferred precursors of this type give rise to peracetic acid on perhydrolysis.

Preferred alkyl fatty peroxyacid precursor compounds of the imide type include the N-,N,N^{1}N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:

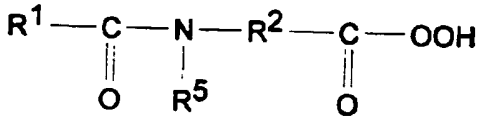


wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. L may be selected from any of the leaving groups described hereinbefore for the analogues having R^1 as an aryl or alkaryl group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

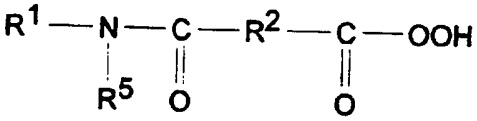
Organic peroxyacids

The compositions may also contain, as oxygen-releasing bleaches, organic peroxyacids, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



or



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group

containing 1 to 10 carbon atoms. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diperoxydodecanedioc acid, diperoxytetra decanedioc acid, diperoxyhexadecanedioc acid, mono- and diperazelaic acid, mono- and diperbrassylic acid, monoperoxy phthalic acid and its magnesium salt, perbenzoic acid, and their salts as disclosed in, for example, EP-A-0341 947.

Total Available Oxygen (AvO) Level

It has been found that, for optimal anti-silver tarnishing performance, the level of available oxygen in the present compositions, measured in units of % available oxygen by weight of the composition, is preferably controlled; the level of available oxygen should hence preferably be in the range from 0.3% to 2.5%, preferably from 0.5% to 1.7%, more preferably from 0.6% to 1.5%, most preferably from 0.7% to 1.2%, measured according to the method described hereunder.

Rate of Release of AvO

The rate of release of available oxygen is preferably also controlled; the rate of release of available oxygen from the compositions herein preferably should be such that, when using the method described hereinafter, the available oxygen is not completely released from the composition until after 3.5 minutes, preferably the available oxygen is released in a time interval of from 3.5 minutes to 10.0 minutes, more preferably from 4.0 minutes to 9.0 minutes, most preferably from 5.0 minutes to 8.5 minutes.

Method for Measuring Level of Total Available Oxygen (AvO) and Rate of Release of AvO in a Detergent Composition

Method

1. A beaker of water (typically 2L) is placed on a stirrer Hotplate, and the stirrer speed is selected to ensure that the product is evenly dispersed through the solution.

2. The detergent composition (typically 8g of product which has been sampled down from a bulk supply using a Pascal sampler), is added and simultaneously a stop clock is started.

3. The temperature control should be adjusted so as to maintain a constant temperature of 20°C throughout the experiment.

4. Samples are taken from the detergent solution at 2 minute time intervals for 20 minutes, starting after 1 minute, and are titrated by the "titration procedure" described below to determine the level of available oxygen at each point.

Titration Procedure

1. An aliquot from the detergent solution (above) and 2ml sulphuric acid are added into a stirred beaker

2. Approximately 0.2g ammonium molybdate catalyst (tetra hydrate form) are added

3. 3mls of 10% sodium iodide solution are added

4. Titration with sodium thiosulphate is conducted until the end point. The end point can be seen using either of two procedures. First procedure consists simply in seeing the yellow iodine colour fading to clear. The second and preferred procedure consists of adding soluble starch when the yellow colour is becoming faint, turning the

solution blue. More thiosulphate is added until the end point is reached (blue starch complex is decolourised).

The level of AvO, measured in units of % available oxygen by weight, for the sample at each time interval corresponds to the amount of titre according to the following equation

$$\frac{\text{Vol } S_2O_3\text{(ml)} \times \text{Molarity } (S_2O_3) \times 8}{\text{Sample mass (g)}}$$

AvO level is plotted versus time to determine the maximum level of AvO, and the rate of release of AvO

Controlled rate of release - means

A means may be provided for controlling the rate of release of oxygen bleach to the wash solution.

Means for controlling the rate of release of the bleach may provide for controlled release of peroxide species to the wash solution. Such means could, for example, include controlling the release of any inorganic perhydrate salt, acting as a hydrogen peroxide source, to the wash solution.

Suitable controlled release means can include coating any suitable component with a coating designed to provide the controlled release. The coating may therefore, for example, comprise a poorly water soluble material, or be a coating of sufficient thickness that the kinetics of dissolution of the thick coating provide the controlled rate of release.

The coating material may be applied using various methods. Any coating material is typically present at a weight ratio of coating material to bleach of from 1:99 to 1:2, preferably from 1:49 to 1:9.

Suitable coating materials include triglycerides (e.g. partially) hydrogenated vegetable oil, soy bean oil, cotton seed oil) mono or

diglycerides, microcrystalline waxes, gelatin, cellulose, fatty acids and any mixtures thereof.

Other suitable coating materials can comprise the alkali and alkaline earth metal sulphates, silicates and carbonates, including calcium carbonate and silicas.

A preferred coating material, particularly for an inorganic perhydrate salt bleach source, comprises sodium silicate of SiO_2 : Na_2O ratio from 1.8 : 1 to 3.0 : 1, preferably 1.8:1 to 2.4:1, and/or sodium metasilicate, preferably applied at a level of from 2% to 10%, (normally from 3% to 5%) of SiO_2 by weight of the inorganic perhydrate salt. Magnesium silicate can also be included in the coating.

Any inorganic salt coating materials may be combined with organic binder materials to provide composite inorganic salt/organic binder coatings. Suitable binders include the C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole of alcohol and more preferably the C_{15}-C_{20} primary alcohol ethoxylates containing from 20 - 100 moles of ethylene oxide per mole of alcohol.

Other preferred binders include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols (PEG) with an average molecular weight of from 600 to 5×10^6 preferably 1000 to 400,000 most preferably 1000 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole. Further examples of binders include the C_{10}-C_{20} mono- and diglycerol ethers and also the C_{10}-C_{20} fatty acids.

Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts are other examples of binders suitable for use herein.

One method for applying the coating material involves agglomeration. Preferred agglomeration processes include the use of any of the organic binder materials described hereinabove. Any conventional agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Molten coating compositions may also be applied either by being poured onto, or spray atomized onto a moving bed of bleaching agent.

Other means of providing the required controlled release include mechanical means for altering the physical characteristics of the bleach to control its solubility and rate of release. Suitable protocols could include compaction, mechanical injection, manual injection, and adjustment of the solubility of the bleach compound by selection of particle size of any particulate component.

Whilst the choice of particle size will depend both on the composition of the particulate component, and the desire to meet the desired controlled release kinetics, it is desirable that the particle size should be more than 500 micrometers, preferably having an average particle diameter of from 800 to 1200 micrometers.

Additional protocols for providing the means of controlled release include the suitable choice of any other components of the detergent composition matrix such that when the composition is introduced to the wash solution the ionic strength environment therein provided enables the required controlled release kinetics to be achieved.

Alkalinity system

The present compositions contain an alkalinity system containing sodium silicate having an SiO_2 : Na_2O ratio of from 1.8 to 3.0, preferably from 1.8 to 2.4, most preferably 2.0, present at a level of from 0.5% to 20%, preferably from 2% to 15%, most preferably from 3% to 12% by weight of

SiO_2. The alkali metal silicate may be in the form of either the anhydrous salt or a hydrated salt.

The alkalinity system also contains sodium metasilicate, present at a level of at least 0.4% SiO_2 by weight. Sodium metasilicate has a nominal SiO_2 : Na_2O ratio of 1.0. The weight ratio of said sodium silicate to said sodium metasilicate, measured as SiO_2, is from 50:1 to 5:4, preferably from 20:1 to 3:2, more preferably from 15:1 to 2:1, most preferably from 10:1 to 5:2.

pH of the compositions

In an essential aspect the present compositions have a pH measured as a 1% solution in distilled water of from 9.0 to 11.5, preferably from 9.5 to 11.2, most preferably from 10.0 to 11.0.

Optional detergent ingredients

In addition to the essential ingredients described hereinabove, the compositions of the invention may be formulated as detergent compositions comprising additional detergent ingredients, preferably selected from water soluble builder compounds, surfactants, heavy metal ion sequestrants, crystal growth inhibitors, enzymes, organic polymeric compounds, corrosion inhibitors, and suds suppressors.

Water-soluble builder compound

The compositions of the present invention may contain as a highly preferred component a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, carbonates, bicarbonates, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less that about 50°C, especially less than about 40°C.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Partially soluble or insoluble builder compound

The compositions of the present invention may less preferably contain a partially soluble or insoluble builder compound. Examples of partially water soluble builders include the crystalline layered silicates as disclosed for example, in EP-A-0164514, DE-A-3417649 and DE-A-3742043. Examples of largely water insoluble builders include the sodium aluminosilicates, including Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeoilte MAP, Zeolite HS and mixtures thereof.

Surfactant

A highly preferred component of the compositions of the invention is a surfactant system comprising surfactant selected from anionic, cationic, nonionic ampholytic and zwitterionic surfactants and mixtures thereof. Preferably the surfactant system comprises low foaming surfactant, which is typically nonionic in character. The surfactant system is typically present at a level of from 0.2% to 30% by weight, more preferably from 0.5% to 10% by weight, most preferably from 1% to 5% by weight of the compositions.

A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31,1981. A listing of surfactants typically included in automatic dishwashing detergent compositions is given for example, in EP-A-0414 549 and PCT Applications No.s WO 93/08876 (attorney's docket no. CM465M) and WO 93/08874 (attorney's docket no. CM595M)..

Nonionic surfactant

Essentially any nonionic surfactants useful for detersive purposes can be included in the compositions. Preferred, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C_6-C_{18} fatty alcohols and C_6-C_{18} mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C_{10}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C_{12}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Heavy metal ion sequestrant

The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion

sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates. Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof.

Crystal growth inhibitor component

The detergent compositions preferably contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 1% by weight of the compositions.

By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

The organo diphosphonic acid is preferably a C_1-C_4 diphosphonic acid, more preferably a C_2 diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

Enzyme

Another optional ingredient useful in the compositions is one or more enzymes. Preferred enzymatic materials include the commercially available lipases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme (lipase) may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions. The lipase may be fungal or bacterial in origin. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is described in Granted European Patent, EP-B-0218272.

An especially preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Enzyme Stabilizing System

Preferred enzyme-containing compositions herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, chlorine bleach scavengers and mixtures thereof. Such stabilizing systems can also comprise reversible enzyme inhibitors, such as reversible protease inhibitors.

Organic polymeric compound

Organic polymeric compounds may be added as preferred components of the compositions in accord with the invention. By organic polymeric compound it is meant essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of molecular weight 2000-10000 and their copolymers with any suitable other monomer units including modified acrylic, fumaric, maleic, itaconic, aconitic, mesaconic, citraconic and methylenemalonic acid or their salts, maleic anhydride, acrylamide, alkylene, vinylmethyl ether, styrene and any mixtures thereof. Preferred are the copolymers of acrylic acid and maleic anhydride having a molecular weight of from 20,000 to 100,000.

Preferred commercially available acrylic acid containing polymers having a molecular weight below 15,000 include those sold under the tradename Sokalan PA30, PA20, PA15, PA10 and Sokalan CP10 by BASF GmbH, and those sold under the tradename Acusol 45N by Rohm and Haas.

Preferred acrylic acid containing copolymers include those which contain as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula -[CR_2-CR_1(CO-O-R_3)]- wherein at least one of the substituents R_1, R_2 or R_3, preferably R_1 or R_2 is a 1 to 4 carbon alkyl or

hydroxyalkyl group, R_1 or R_2 can be a hydrogen and R_3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_1 is methyl, R_2 is hydrogen (i.e. a methacrylic acid monomer). The most preferred copolymer of this type has a molecular weight of 3500 and contains 60% to 80% by weight of acrylic acid and 40% to 20% by weight of methacrylic acid.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Lime soap dispersant compound

The compositions of the invention may contain a lime soap dispersant compound, preferably present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. Preferred lime soap disperant compounds are disclosed in PCT Application No. WO93/08877 (attorney's docket no. CM466M).

Suds suppressing system

The compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl and alcanol antifoam compounds. Preferred suds suppressing systems and antifoam compounds are disclosed in PCT Application No. WO93/08876 (attorney's docket no. CM465M) and copending European Application No. 93870132.3 (attorney's docket no. CM562F).

Polymeric dye transfer inhibiting agents

The compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

Corrosion inhibitor

The compositions may contain corrosion inhibitors such as benzotriazole and paraffin. Suitable corrosion inhibitors are described in PCT Application No. WO94/07981 and copending European Application No. EP 93202095.1 (attorney's docket no. CM571F).

Form of the compositions

The compositions of the invention can be formulated in any desirable form such as powders, granulates, pastes, liquids, gels and tablets, granular forms being preferred.

The bulk density of the granular detergent compositions in accordance with the present invention is typically of at least 650 g/litre, more usually at least 700 g/litre and more preferably from 800 g/litre to 1200 g/litre.

The particle size of the components of granular compositions in accordance with the invention should preferably be such that no more that 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

Generally, if the compositions are in liquid form the liquid should be thixotropic (ie; exhibit high viscosity when subjected to low stress and lower viscosity when subjected to high stress), or at least have very high viscosity, for example, of from 1,000 to 10,000,000 centipoise.

Washing method

Any suitable methods for washing or cleaning soiled tableware, including soiled patterned glassware and silverware, are envisaged including machine dishwashing methods.

Machine dishwashing method

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a machine dishwashing composition in accord with the invention. By an effective amount of the machine dishwashing composition it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

In the detergent compositions, the abbreviated component identifications have the following meanings:

Nonionic	:	C_{13}-C_{15} mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF Gmbh (low foaming)
Metasilicate	:	Sodium metasilicate (SiO_2:Na_2O ratio = 1.0)
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O ratio = 2.0)
Carbonate	:	Anhydrous sodium carbonate

Phosphate	:	Sodium tripolyphosphate
480N	:	Random copolymer of 3:7 acrylic/methacrylic acid, average molecular weight about 3,500
Citrate	:	Tri-sodium citrate dihydrate
PB1	:	Anydrous sodium perborate monohydrate
PB4	:	Anhydrous sodium perborate tetrahydrate
TAED	:	Tetraacetyl ethylene diamine
DETPMP	:	Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the tradename Dequest 2060
HEDP	:	Ethane 1-hydroxy-1,1-diphosphonic acid
Paraffin	:	Paraffin oil sold under the tradename Winog 70 by Wintershall.
Protease	:	Proteolytic enzyme sold under the tradename Savinase by Novo Industries A/S (approx 2% enzyme activity).
Amylase	:	Amylolytic enzyme sold under the tradename Termamyl 60T by Novo Industries A/S (approx 0.9% enzyme activity)
BSA	:	Amylolytic enzyme sold under the tradename LE17 by Novo Industries A/S (approx 1% enzyme activity)
Sulphate	:	Anhydrous sodium sulphate.

pH : Measured as a 1% solution in distilled water at 20°C.

In the following examples all levels of enzyme quoted are expressed as % active enzyme by weight of the composition.

Example 1

The following machine dishwashing detergent compositions were prepared (parts by weight). Compositions A and E are comparative compositions, compositions B to D and F and G are in accord with the invention.

	A	B	C	D	E	F	G
Citrate	15.0	15.0	15.0	-	-	_	15.0
480N	6.0	6.0	6.0	-	-	4.0	6.0
Carbonate	20.0	17.5	17.5	7.55	-	-	17.5
Phosphate	-	-	-	53.0	53.0	53.0	-
Silicate (as SiO_2)	8.0	8.0	6.0	8.0	8.0	14.0	8.0
Metasilicate (as SiO_2)	-	1.25	2.5	2.0	-	5.0	1.2
PB1 (AvO)	0.3	0.3	0.3	1.2	1.2	1.2	0.3
PB4 (AvO)	0.9	0.9	0.9	-	-	-	0.9
TAED	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Protease	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Amylase	0.03	0.03	0.03	0.03	0.03	0.03	0.03
BSA	-	-	-	-	-	-	0.03
DETPMP	0.13	0.13	0.13	-	-	-	0.13

HEDP	1.0	1.0	1.0	-	-	-	1.0
Nonionic	2.0	2.0	2.0	2.0	2.0	2.0	2.0
misc inc sulphate/moisture to balance							
pH (1% solution)	10.7	10.7	10.8	10.6	10.3	11.0	10.7

Comparative testing - silver tarnishing

The silver tarnish prevention performance of Composition B, in accord with the invention was compared to that of comparative Composition A using the following twenty cycle test procedure. A set of three silver spoons were placed in the cutlery basket of each of four Phillips (tradename) machine dishwashers. Twenty grams of background soil, comprising 1 part by weight of each of Prince's (tradename) tinned stewing steak, Heinz (tradename) tinned baked beans and Ambrosia (tradename) tinned creamed rice, well mixed together, was added to each dishwasher by placing the soil in a 50 cm^3 plastic beaker which was stood inverted in the upper rack of the dishwasher. A spike comprising 10 cm^3 of 0.262% by weight $CaCl_2$. $6H_2O$ solution was added by pipette to the bottom of each dishwasher. The 65°C wash setting was selected, the wash process comprising main wash and rinse cycles. 20 grams of each composition was employed for each complete wash process. The feed water hardness was 8° Clark Hardness (114.3 ppm $CaCO_3$ equivalent). Each set of three spoons was washed five times in each of the four machines (ie: 20 complete wash + rinse cycles).

At the end of the final wash process the spoons were removed and then graded for silver tarnishing. The grading was performed by 4 expert graders and the results averaged for each of the four sets of three spoons. Grading was through visual inspection according to the following scale :

0 = no tarnish (shiny silver)
1 = very slight tarnish
2 = tarnish
3 = very tarnished
4 = severe tarnish (black coverage)

Results were as follows : (average of the 4 gradings from the panellists)

Composition A	Composition B
2.0	0.5

Comparison of the grade obtained for product A with that obtained for product B shows that less silver tarnishing is obtained for Composition B in accord with the invention.

Comparative testing - glassware pattern protection

The glass pattern protection performance of Compositions B to D and F, in accord with the invention was compared to that of comparative Compositions A and E using the following thirty-cycle test procedure.

A set of six 200ml household glasses having various overlaid glass patterns, including representations of fruits, flowers and cartoon characters, were placed in the upper rack of each of six Bosch Siemens SMS6032 (tradename) machine dishwashers. The 65°C wash setting was selected, the wash process comprising main wash and rinse cycles. 26 grams of each composition was employed for each complete wash process. The feed water hardness was 8° Clark Hardness (114.3 ppm $CaCO_3$ equivalent). Dishwasher salt was employed to reduce the in wash water

hardness to about 2° Clark Hardness (28.6 ppm $CaCO_3$ equivalent). Each set of six glasses was washed five times in each of the six machines (ie: 30 complete wash + rinse cycles).

At the end of the final wash process the glasses were removed and then graded for glass pattern corrosion effects. The grading was performed by 4 expert graders and the results averaged for each of the six sets of six glasses. Grading was through visual inspection according to the following scale :

1 = no pattern damage
2 = very slight pattern damage (visible on close inspection)
3 = noticeable pattern damage
4 = very noticeable pattern damage
5 = severe pattern damage

Results were as follows : (average of the 4 gradings from the panellists)

A	B	C	D	E	F
2.5	2.0	1.5	3.0	4.0	2.0

The pattern protection profile of Compositions B and C is hence seen to be better than that of related comparative Composition A. Similarly, the pattern protection profile of Compositions D and F is better than that of related comparative Composition E.

Comparative testing - calcium carbonate film formation prevention

The calcium carbonate film formation prevention performance in both hard and soft water conditions of Composition B, in accord with the invention was compared to that of comparative Composition A using the following test procedures.

'Soft water'

A set of six clear 200ml household glasses were placed in the upper rack of each of five Bosch Siemens SMS6032 (tradename) machine dishwashers. The 65°C wash setting was selected, the wash process comprising main wash and rinse cycles. 20 grams of each detergent composition was employed for each complete wash process. The feed water hardness was 8° Clark Hardness (114.3 ppm $CaCO_3$ equivalent). A dishwasher salt was employed to reduce the in wash water hardness to about 2° Clark Hardness (28.6 ppm $CaCO_3$ equivalent). Each set of six glasses was washed either twenty or sixty times in each of the five machines (ie: either 100 or 300 complete wash + rinse cycles).

'Hard water'

Procedure as for the 'soft water' test, but the feed water hardness was 17° Clark Hardness (242.9 ppm $CaCO_3$ equivalent) and the wash water hardness was hence also correspondingly higher at about 5° Clark Hardness (71.5 ppm $CaCO_3$ equivalent). Only a 100 complete wash cycle test was run.

Grading

At the end of the final wash process the glasses were removed and then graded for the presence of calcium carbonate film. The grading was performed by 4 expert graders and the results averaged for each of the five sets of six glasses. Grading was through visual inspection according to a 10-point grading scale, where 10 means no filming and 1 means severe filming.

Results were as follows : (average of the 4 gradings from the panellists)

	A	B
'Soft water' (100 cycles)	9.0	8.0
'Soft water' (300 cycles)	8.0	7.0
'Hard water' (100 cycles)	7.0	6.2

The calcium carbonate film deposition profile of Composition B is hence seen to be better than that of related comparative Composition A.

CLAIMS

1. A bleaching composition, adapted for use in a machine dishwashing method, containing

   (a) an oxygen-releasing bleaching system;

   (b) sodium silicate having an $SiO_2 : Na_2O$ ratio of from 1.8 to 3.0, present at a level of from 0.5% to 20% SiO_2 by weight ; and

   (c) sodium metasilicate, present at a level of at least 0.4% SiO_2 by weight

   wherein the weight ratio of said sodium silicate to said sodium metasilicate, measured as SiO_2, is from 50:1 to 3:2 and wherein the pH of a 1% solution of said composition measured at 20°C is from 9.0 to 11.5.

2. A bleaching composition according to Claim 1 wherein said sodium silicate is present at a level of from 3% to 12% by weight of SiO_2.

3. A bleaching composition according to either of Claims 1 or 2 wherein the weight ratio of said sodium silicate to said sodium metasilicate, measured as SiO_2, is from 15:1 to 2:1.

4. A bleaching composition according to any of Claims 1 to 3 wherein said sodium silicate has an $SiO_2 : Na_2O$ ratio of from 1.8 to 2.4, preferably 2.0.

5. A bleaching composition according to any of Claims 1 to 4 wherein the pH of a 1% solution of said composition measured at 20°C is from 10.0 to 11.0.

6. A bleaching composition according to any of Claims 1 to 5 wherein said oxygen-releasing bleaching system comprises a hydrogen peroxide source and a peroxyacid bleach precursor compound.

7. A bleaching composition according to Claim 6 wherein said hydrogen peroxide source comprises an inorganic perhydrate salt.

8. A bleaching composition according to Claim 7 wherein said inorganic perhydrate salt is coated with a coating material comprising a proportion of said sodium silicate and/or said sodium metasilicate at a level of from 2% to 10% of SiO_2 by weight of the inorganic perhydrate salt.

9. A detergent composition according to any of Claims 1 to 8 containing:

   (a) from 10% to 70% by weight of the composition of a water soluble builder compound; and

   (b) from 0.5% to 10% by weight of the composition of a low foaming surfactant system.

Patents Act 1977 Examiner's report to the Comptroller under Section 17 44 (The Search report)	Application number GB 9424010.8
Relevant Technical Fields (i) UK Cl (Ed.M) D1P (PCBD, PCBE, PDS, PDV, PDX); C5D (DHE, DHX, DHZ) (ii) Int Cl (Ed.5) D06L 3/02, C11D 3/08, 3/395	Search Examiner MR P DAVEY Date of completion of Search 17 JANUARY 1995
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE: WPI	Documents considered relevant following a search in respect of Claims :- 1-9

Categories of documents

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A:	Document indicating technological background and/or state of the art.	**&:**	Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A	WO 92/13061 A1 (ECOLAB) see eg Table 1	1 at least

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